

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup>:</b> <b>C11D 17/06, 11/00</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 95/06109</b> <b>(43) International Publication Date:</b> <b>2 March 1995 (02.03.95)</b>
<b>(21) International Application Number:</b> <b>PCT/US94/08957</b> <b>(22) International Filing Date:</b> <b>9 August 1994 (09.08.94)</b> <b>(30) Priority Data:</b> 08/113,572                      27 August 1993 (27.08.93)      US 08/283,131                      3 August 1994 (03.08.94)      US <b>(71) Applicant:</b> <b>THE PROCTER &amp; GAMBLE COMPANY</b> <b>[US/US]; One Procter &amp; Gamble Plaza, Cincinnati, OH</b> <b>45202 (US).</b> <b>(72) Inventors:</b> <b>CAPECI, Scott, William; 3285 Citation Lane, North</b> <b>Bend, OH 45052 (US). OSBORN, James, William; 16</b> <b>West Hollister Street, Cincinnati, OH 45219 (US). AN-</b> <b>GELL, Adrian, John, Waynforth; Nieuwelaan 121, B-1853</b> <b>Strombeek-Bever (BE). DIJK, Paul, Van; Leuvensebaan</b> <b>226, B-2580 Putte (BE).</b> <b>(74) Agents:</b> <b>REED, T., David et al.; The Procter &amp; Gamble</b> <b>Company, 5299 Spring Grove Avenue, Cincinnati, OH</b> <b>45217 (US).</b>	<b>(81) Designated States:</b> <b>CA, CN, JP, European patent (AT, BE, CH,</b> <b>DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</b>  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>	
<b>(54) Title:</b> <b>PROCESS FOR MAKING HIGH DENSITY DETERGENT AGGLOMERATES</b>  <b>(57) Abstract</b>  A process for preparing high density detergent agglomerates having a density of at least 650 g/l is provided. The process comprises the steps of: (a) charging a viscous surfactant paste into a mixer/densifier wherein the surfactant paste has a viscosity of from about 5,000 cps to about 100,000 cps and contains at least about 5 % water; (b) adding from about 1 % to about 70 % of an anhydrous material into the surfactant paste just prior to entrance into the mixer/densifier to absorb at least a minor amount of the water from the surfactant paste; and (c) agglomerating the surfactant paste and the anhydrous material in the mixer/densifier so as to form detergent agglomerates having a density of at least about 650 g/l. The detergent agglomerates have high surfactant levels.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

## PROCESS FOR MAKING HIGH DENSITY DETERGENT AGGLOMERATES

5

### CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part application of Serial No. 08/113,572, filed August 27, 1993, now allowed.

10

### FIELD OF THE INVENTION

The present invention generally relates to a process for producing detergent agglomerates. More particularly, the invention is directed to a process during which high density detergent agglomerates are produced using an anhydrous material which is hydratable in that it can absorb a sufficient amount of water so as to facilitate agglomeration. The process produces free flowing, high surfactant level, detergent agglomerates having a density of at least 650 g/l and are thus particularly useful in producing low dosage detergent compositions.

### BACKGROUND OF THE INVENTION

Recently, there has been considerable interest within the detergent industry for laundry detergents which are "compact" and therefore, have low dosage volumes. To facilitate production of these so-called low dosage detergents, many attempts have been made to produce high bulk density detergents, for example with a density of 600 g/l or higher. The low dosage detergents are currently in high demand as they conserve resources and can be sold in small packages which are more convenient for consumers, especially in households where there is a premium on storage space.

Generally, there are two primary types of processes by which detergent granules or powders can be prepared. The first type of process involves spray-drying an aqueous detergent slurry in a spray-drying tower to produce highly porous detergent granules. In the second type of process, the various detergent components are dry mixed just prior to agglomeration with a binder, such as a nonionic surfactant. In the latter process in which the starting detergent materials are mixed together prior to agglomeration, there has been difficulty in producing consistent, free flowing, detergent agglomerates having the desired high density, especially when there is a high amount of binder present e.g. about 10% or higher.

The art is replete with disclosures of detergent compositions containing anhydrous materials such as carbonates and sulfates. For example, Kaminsky (commonly assigned), U.S. Patent No. 4,487,710, discloses a granular detergent composition containing an anionic surfactant, an anhydrous material such as carbonates and sulfates, and an ethoxylated surfactant solubility aid. While the detergent composition is produced by agglomeration, it is not produced from a viscous surfactant paste, typically having a high water content e.g. 10% or higher. In the past, there has

been difficulty in producing free flowing detergent agglomerates from such a surfactant paste which has been agglomerated.

Further, there has also been difficulty in attaining high levels of surfactant in the resulting detergent agglomerates, a feature which facilitates production of low dosage detergents. More particularly, any increase in the density of granules produced by way of conventional spray drying techniques is limited by the relative amount of surfactant required to be passed through the spray drying tower. By providing a detergent agglomerate admix having a high surfactant level, the amount of surfactant passed through the spray drying tower can be reduced, thereby increasing the density of the exiting granules and ultimately the finished detergent. Thus, it would be desirable to have a process by which detergent agglomerates having higher surfactant levels can be produced.

The art is also replete with disclosures of agglomerating detergent compositions, some of which contain anhydrous materials. For example, Curtis, European patent application No. 451,894 (Unilever), discloses a process for preparing high density detergent granules by using two mixers in series. In particular, an admix of starting detergent materials are fed into a high speed mixer/densifier after which the materials are fed into a moderate speed mixer/densifier to increase the bulk density further. Thus, Curtis initially requires a high speed mixer/densifier to pulverize the detergent granules and then a second moderate speed mixer/densifier to increase the density to the desired level. Again, the Curtis process does not entail agglomerating a viscous surfactant paste.

Accordingly, despite the above-described disclosures in the art, it would be desirable to have a process for producing high density detergent agglomerates having a density of at least 650 g/l from a viscous surfactant paste among other starting detergent components. It would also be desirable for such a process to produce detergent agglomerates having higher levels of surfactant to aid in the production of low dosage detergents and admixes therefor.

#### SUMMARY OF THE INVENTION

The present invention meets the aforementioned needs in the art by providing a process which produces high density, free flowing detergent agglomerates having a density of at least 650 g/l from a highly viscous surfactant paste. The process achieves the desired high density, free flowing detergent agglomerates without unnecessary process parameters, such as relatively high operating temperatures which increase manufacturing costs. The resulting high density detergent agglomerates produced by the present invention also attain high surfactant levels which facilitate use as a detergent or as a detergent admix.

As used herein, the term "agglomerates" refers to particles formed by agglomerating detergent granules or particles which typically have a smaller mean particle size than the formed agglomerates. As used herein, the phrase "at least a minor amount" of water means an amount sufficient to aid in agglomeration, typically on the order of 0.5% to about 10% by weight of the total amount of water contained in the mixture of all starting components. All percentages used

herein are expressed as "percent-by-weight" unless indicated otherwise. All viscosities described herein are measured at 70°C and at shear rates between about 10 to 50 sec<sup>-1</sup>, preferably at 25 sec<sup>-1</sup>.

In accordance with one aspect of the invention, a process for preparing high density detergent agglomerates is provided. The process for preparing high density detergent agglomerates comprises the steps of: (a) charging a viscous surfactant paste into a mixer/densifier wherein the surfactant paste has a viscosity of from about 5,000 cps to about 100,000 cps and contains from about 70% to 95%, by weight of said surfactant paste, of a deterative surfactant and the balance water; (b) adding from about 1% to about 70% of an anhydrous material selected from the group consisting of carbonates, sulfates, carbonate/sulfate complexes, tripolyphosphates, tetrasodium pyrophosphate, citrates, aluminosilicates, cellulose-based materials and organic synthetic polymeric absorbent gelling materials into said surfactant paste just prior to entrance into said mixer/densifier to absorb at least a minor amount of said water from said surfactant paste; and (c) agglomerating said surfactant paste and said anhydrous material by treating said surfactant paste and said anhydrous material initially in a high speed mixer/densifier and subsequently in a moderate speed mixer/densifier so as to form detergent agglomerates having a density of at least about 650 g/l.

In accordance with another aspect of the invention, another process for preparing high density detergent agglomerates is provided. The process comprises the steps of: (a) forming a viscous surfactant paste wherein the surfactant paste has a viscosity of from about 5,000 cps to about 100,000 cps and contains from about 70% to 95%, by weight of the surfactant paste, of a deterative surfactant and the balance water; (b) agglomerating the surfactant paste by treating the surfactant paste initially in a high speed mixer/densifier and subsequently in a moderate speed mixer/densifier to form detergent agglomerates; and (c) adding from about 1% to about 70% by weight of an anhydrous material selected from the group consisting of carbonates, sulfates, carbonate/sulfate complexes, tripolyphosphates, tetrasodium pyrophosphate, citrates, aluminosilicates, cellulose-based materials and organic synthetic polymeric absorbent gelling materials into said high speed mixer/densifier to absorb at least a minor amount of the water such that the detergent agglomerates are free flowing and have a density of at least about 650 g/l.

Accordingly, it is an object of the present invention to provide a process for producing high density, free flowing detergent agglomerates with a density of at least 650 g/l. It is also an object of the invention to provide a process by which such high density agglomerates can be produced from a viscous surfactant paste and other conventional detergent starting ingredients, wherein the agglomerates contain higher surfactant levels. These and other objects, features and attendant advantages of the present invention will become apparent to those skilled in the art from a reading of the following detailed description of the preferred embodiment and the appended claims.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The present invention is directed to a process which produces free flowing, high density detergent agglomerates having a density of at least 650 g/l. The process produces high density

detergent agglomerates from a highly viscous surfactant paste having a relatively high water content, typically at least about 5%, to which an anhydrous material is added to absorb such water. It is the excess water in the surfactant which is believed to hinder agglomeration. Generally, the present process is used in the production of low dosage detergents whereby the resulting detergent  
5 agglomerates can be used as a detergent or as a detergent additive. In particular, the process can be used to form "high active" (i.e. high surfactant level) detergent agglomerates which are used as an admix for purposes of enhancing the active levels in granular low dosage detergents and thereby allow for more compact detergents. It should be understood that the process described herein can be continuous or batch depending upon the desired application.

10

#### Process

In the first step of the process, starting detergent materials are fed into a mixer/densifier for agglomeration. In another embodiment of the invention which is discussed more fully below, the starting detergent materials can be initially fed into a mixer or pre-mixer (e.g. a conventional screw extruder or other similar mixer) prior to agglomeration, after which the mixed detergent materials  
15 are fed into mixer/densifiers as described herein for agglomeration. The anhydrous materials described herein can be added either in the extruder (pre-mixer) or in the mixer/densifier during the agglomeration step.

To achieve the desired density of 650 g/l, the agglomeration step can be carried forth initially in a high speed mixer/densifier after which a moderate speed mixer/densifier can follow,  
20 wherein the starting detergent materials are agglomerated and densified to produce particles having a density of at least 650 g/l and, more preferably from about 700 g/l to about 800 g/l. The nature and composition of the entering or starting detergent materials can vary as described in detail hereinafter. Preferably, the mean residence time of the starting detergent materials in the high speed mixer/densifier (e.g. Lodige Recycler CB30) is from about 1 to 30 seconds while the residence  
25 time in low or moderate speed mixer/densifier (e.g. Lodige Recycler KM 300 "Ploughshare") is from about 0.25 to 10 minutes. Alternatively, the agglomeration step of the process contemplates achieving the desired density of the starting detergent materials by agglomeration in a single moderate speed mixer/densifier wherein the residence time is increased, for example, up to about 15 minutes.

30

The starting detergent materials preferably include a highly viscous surfactant paste, the components of which are described more fully hereinafter. For purposes of facilitating agglomeration, an anhydrous material is added to the starting detergent materials including the viscous surfactant paste just prior to or, during agglomeration. In the past, agglomeration of large amounts of viscous surfactant paste having a viscosity of from about 5,000 cps to about 100,000 cps  
35 and containing at least about 5% water has resulted in detergent agglomerates which are unacceptably large, sticky and lumpy. It has now been found that the inclusion of the

aforementioned anhydrous material during or just prior to agglomeration eliminates or substantially minimizes such problems.

The present process entails mixing from about 1% to about 70%, more preferably from about 5% to about 50% and, most preferably from about 5% to about 20%, by weight of an  
5 anhydrous material into the mixer/densifier to absorb at least a minor amount of the water from the surfactant paste. Thereafter, the surfactant paste, anhydrous material and other detergent materials are agglomerated in the mixer/densifier so as to form detergent agglomerates having a density of at least about 650 g/l. While not intending to be limited by theory, it is believed that the free flowing, high density detergent agglomerates produced by the present invention is attributed to the  
10 absorption of the excess water typically contained in the viscous surfactant paste by the anhydrous material during or just prior to agglomeration.

As mentioned previously, the anhydrous material can be added to the starting detergent materials prior to agglomeration. In particular, the process comprises the steps of initially forming a viscous surfactant paste to which other detergent materials as described hereinafter can be added.  
15 This, for example, can be completed in a twin-screw extruder (residence time of five seconds to 300 seconds) to insure complete mixing of the starting ingredients and provide ample residence time to complete the dehydration. The anhydrous material is then mixed into the surfactant paste in the extruder, after which the materials from the extruder are immediately and continuously fed into a mixer/densifier for agglomeration. The resulting detergent agglomerates are free flowing, have  
20 high surfactant levels and have the desired high density.

The detergent agglomerates produced by the process preferably have a surfactant level of from about 25% to about 55%, more preferably from about 35% to about 55% and, most preferably from about 45% to about 55%. Such detergent agglomerates are particularly useful in the production of low dosage detergents. The particle porosity of the resulting detergent agglomerates  
25 produced according to the process of the invention is preferably in a range from about 5% to about 20%, more preferably at about 10%. In addition, an attribute of dense or densified agglomerates is the relative particle size. The present process typically provides detergent agglomerates having a mean particle size of from about 400 microns to about 700 microns, and more preferably from about 400 microns to about 600 microns. As used herein, the phrase "mean particle size" refers to  
30 individual agglomerates and not individual particles or detergent granules. The combination of the above-referenced porosity and particle size results in agglomerates having density values of 650 g/l and higher. Such a feature is especially useful in the production of low dosage laundry detergents as well as other granular compositions such as dishwashing compositions.

#### Optional Process Steps

35 The process can comprises the step of spraying an additional binder in the mixer/densifier(s) used in the agglomeration step to facilitate production of the desired detergent agglomerates. A binder is added for purposes of enhancing agglomeration by providing a "binding"

or "sticking" agent for the detergent components. The binder is preferably selected from the group consisting of water, anionic surfactants, nonionic surfactants, polyethylene glycol, polyacrylates, citric acid and mixtures thereof. Other suitable binder materials including those listed herein are described in Beerse et al, U.S. Patent No. 5,108,646 (Procter & Gamble Co.), the disclosure of which is incorporated herein by reference.

Another optional step contemplated by the present process includes conditioning the detergent agglomerates by either drying or adding a coating agent to improve flowability after they exit the mixer/densifier(s) used in agglomeration. This further enhances the condition of the detergent agglomerates for use as an additive or to place them in shippable or packagable form. Those skilled in the art will appreciate that a wide variety of methods may be used to dry as well as cool the exiting detergent agglomerates without departing from the scope of the invention. By way of example, apparatus such as a fluidized bed can be used for drying while an airlift can be used for cooling should it be necessary.

#### Anhydrous Material

The anhydrous material used in the present process is present in an amount from about 1% to about 70%, more preferably from about 5% to about 50%, and most preferably from about 5% to about 20%. As used herein, the term "anhydrous material" means any hydratable material which is capable of absorbing water rapidly. Preferably, the anhydrous material is selected from the group consisting of carbonates, sulfates, carbonate/sulfate complexes, and mixtures thereof. While not intending to be limiting, other suitable anhydrous materials include powdered tripolyphosphate, powdered tetrasodium pyrophosphate, citrate, powdered carbonates such as calcium carbonate, powdered sulfates and mixtures thereof. Further, aluminosilicates disclosed in Corkill et al, U.S. Patent No. 4,605,509 (Procter & Gamble), the disclosure of which is incorporated herein by reference, typically which have been overdried are suitable for use herein. Also, the anhydrous material can be selected from group consisting of absorbent gelling materials, cellulose-based materials and combinations thereof. Suitable absorbent gelling materials are disclosed in Brandt et al, U.S. Patent Reissue No. 32,649 (commonly assigned), the disclosure of which is incorporated herein by reference. Suitable cellulose-based materials are disclosed in Herron, U.S. Patent No. 5,183,707 and Herron et al, U.S. Patent No. 5,137,537, the disclosures of which are incorporated by reference. Most preferably, magnesium sulfate has been found to be effective in the process described herein.

#### Surfactant Paste

The viscous surfactant paste used in the process has a viscosity of from about 5,000 cps to about 100,000 cps, more preferably from about 7,500 cps to about 75,000 cps, and contains at least about 5% water, more preferably at least about 10% or more water. As mentioned previously, the viscosity is measured at 70°C and at shear rates of about 10 to 50 sec.<sup>-1</sup>, preferably at 25 sec.<sup>-1</sup>. Furthermore, the surfactant comprises from about 70% to about 95%, more preferably from about

75% to about 85% of a deterative surfactant, and the balance water and other conventional detergent ingredients.

The surfactant can be selected from anionic, nonionic, zwitterionic, ampholytic and cationic classes and compatible mixtures thereof. Detergent surfactants useful herein are described in U.S. Patent 3,664,961, Norris, issued May 23, 1972, and in U.S. Patent 3,919,678, Laughlin et al., issued December 30, 1975, both of which are incorporated herein by reference. Useful cationic surfactants also include those described in U.S. Patent 4,222,905, Cockrell, issued September 16, 1980, and in U.S. Patent 4,239,659, Murphy, issued December 16, 1980, both of which are also incorporated herein by reference. Of the surfactants, anionics and nonionics are preferred and anionics are most preferred.

The following are representative examples of detergent surfactants useful in the present surfactant paste. Water-soluble salts of the higher fatty acids, i.e., "soaps", are useful anionic surfactants in the compositions herein. This includes alkali metal soaps such as the sodium, potassium, ammonium, and alkylammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms, and preferably from about 12 to about 18 carbon atoms. Soaps can be made by direct saponification of fats and oils or by the neutralization of free fatty acids. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap.

Additional anionic surfactants which suitable for use herein include the water-soluble salts, preferably the alkali metal, ammonium and alkylammonium salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups.) Examples of this group of synthetic surfactants are the sodium and potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols ( $C_{8-18}$  carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil; and the sodium and potassium alkylbenzene sulfonates in which the alkyl group contains from about 9 to about 15 carbon atoms, in straight chain or branched chain configuration, e.g., those of the type described in U.S. Patents 2,220,099 and 2,477,383. Especially valuable are linear straight chain alkylbenzene sulfonates in which the average number of carbon atoms in the alkyl group is from about 11 to 13, abbreviated as  $C_{11-13}$  LAS.

Other anionic surfactants suitable for use herein are the sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates; sodium or potassium of ethylene oxide per molecule and wherein the alkyl groups contain from about 8 to about 12 carbon atoms; and sodium or potassium salts of alkyl ethylene oxide ether sulfates containing about 1 to about 10 units of ethylene oxide per molecule and wherein the alkyl group contains from about 10 to about 20 carbon atoms.

In addition, suitable anionic surfactants include the water-soluble salts of esters of alpha-sulfonated fatty acids containing from about 6 to 20 carbon atoms in the fatty acid group and from about 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxyalkane-1-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; water-soluble salts of olefin and paraffin sulfonates containing from about 12 to 20 carbon atoms; and beta-alkyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

Preferred anionic surfactants are C<sub>10-18</sub> linear alkylbenzene sulfonate and C<sub>10-18</sub> alkyl sulfate. If desired, low moisture (less than about 25% water) alkyl sulfate paste can be the sole ingredient in the surfactant paste. Most preferred are C<sub>10-18</sub> alkyl sulfates, linear or branched, and any of primary, secondary or tertiary. A preferred embodiment of the present invention is wherein the surfactant paste comprises from about 20% to about 40% of a mixture of sodium C<sub>10-13</sub> linear alkylbenzene sulfonate and sodium C<sub>12-16</sub> alkyl sulfate in a weight ratio of about 2:1 to 1:2. Another preferred embodiment of the detergent composition includes a mixture of C<sub>10-18</sub> alkyl sulfate and C<sub>10-18</sub> alkyl ethoxy sulfate in a weight ratio of about 80:20.

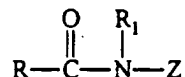
Water-soluble nonionic surfactants are also useful in the instant invention. Such nonionic materials include compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. The length of the polyoxyalkylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Suitable nonionic surfactants include the polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to 15 carbon atoms, in either a straight chain or branched chain configuration, with from about 3 to 12 moles of ethylene oxide per mole of alkyl phenol. Included are the water-soluble and water-dispersible condensation products of aliphatic alcohols containing from 8 to 22 carbon atoms, in either straight chain or branched configuration, with from 3 to 12 moles of ethylene oxide per mole of alcohol.

An additional group of nonionics suitable for use herein are semi-polar nonionic surfactants which include water-soluble amine oxides containing one alkyl moiety of from about 10 to 18 carbon atoms and two moieties selected from the group of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of about 10 to 18 carbon atoms and two moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to 3 carbon atoms.

Preferred nonionic surfactants are of the formula  $R^1(OC_2H_4)_nOH$ , wherein  $R^1$  is a  $C_{10}$ - $C_{16}$  alkyl group or a  $C_8$ - $C_{12}$  alkyl phenyl group, and  $n$  is from 3 to about 80. Particularly preferred are condensation products of  $C_{12}$ - $C_{15}$  alcohols with from about 5 to about 20 moles of ethylene oxide per mole of alcohol, e.g.,  $C_{12}$ - $C_{13}$  alcohol condensed with about 6.5 moles of ethylene oxide per mole of alcohol.

Additional suitable nonionic surfactants include polyhydroxy fatty acid amides of the formula



wherein  $R$  is a  $C_9$ - $C_{17}$  alkyl or alkenyl,  $R_1$  is a methyl group and  $Z$  is glyceryl derived from a reduced sugar or alkoxyated derivative thereof. Examples are  $N$ -methyl  $N$ -1-deoxyglucityl cocoamide and  $N$ -methyl  $N$ -1-deoxyglucityl oleamide. Processes for making polyhydroxy fatty acid amides are known and can be found in Wilson, U.S. Patent No. 2,965,576 and Schwartz, U.S. Patent No. 2,703,798, the disclosures of which are incorporated herein by reference.

Ampholytic surfactants include derivatives of aliphatic or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic moiety can be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and at least one aliphatic substituent contains an anionic water-solubilizing group.

Zwitterionic surfactants include derivatives of aliphatic, quaternary, ammonium, phosphonium, and sulfonium compounds in which one of the aliphatic substituents contains from about 8 to 18 carbon atoms.

Cationic surfactants can also be included in the present invention. Cationic surfactants comprise a wide variety of compounds characterized by one or more organic hydrophobic groups in the cation and generally by a quaternary nitrogen associated with an acid radical. Pentavalent nitrogen ring compounds are also considered quaternary nitrogen compounds. Suitable anions are halides, methyl sulfate and hydroxide. Tertiary amines can have characteristics similar to cationic surfactants at washing solution pH values less than about 8.5. A more complete disclosure of these and other cationic surfactants useful herein can be found in U.S. Patent 4,228,044, Cambre, issued October 14, 1980, incorporated herein by reference.

Cationic surfactants are often used in detergent compositions to provide fabric softening and/or antistatic benefits. Antistatic agents which provide some softening benefit and which are preferred herein are the quaternary ammonium salts described in U.S. Patent 3,936,537, Baskerville, Jr. et al., issued February 3, 1976, the disclosure of which is incorporated herein by reference.

#### Optional Detergent Components

The starting detergent ingredients of the present process can, and preferably do, also comprise a detergent builder. Builders are generally selected from the various water-soluble, alkali metal, ammonium or substituted ammonium phosphates, polyphosphates, phosphonates.

polyphosphonates, carbonates, silicates, borates, polyhydroxy sulfonates, polyacetates, carboxylates, and polycarboxylates. Preferred are the alkali metal, especially sodium, salts of the above.

Preferred for use herein are the phosphates, carbonates, silicates, C<sub>10-18</sub> fatty acids, polycarboxylates, and mixtures thereof. More preferred are sodium triphosphosphate, tetrasodium pyrophosphate, citrate, tartrate mono- and di-succinates, sodium silicate, and mixtures thereof (see below).

Specific examples of inorganic phosphate builders are sodium and potassium triphosphosphate, pyrophosphate, polymeric metaphosphate having a degree of polymerization of from about 6 to 21, and orthophosphates. Examples of polyphosphonate builders are the sodium and potassium salts of ethylene diphosphonic acid, the sodium and potassium salts of ethane 1-hydroxy-1, 1-diphosphonic acid and the sodium and potassium salts of ethane, 1,1,2-triphosphonic acid. Other phosphorus builder compounds are disclosed in U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,422,137; 3,400,176 and 3,400,148, all of which are incorporated herein by reference.

Examples of nonphosphorus, inorganic builders are sodium and potassium carbonate, bicarbonate, sesquicarbonate, tetraborate decahydrate, and silicates having a weight ratio of SiO<sub>2</sub> to alkali metal oxide of from about 0.5 to about 4.0, preferably from about 1.0 to about 2.4. Water-soluble, nonphosphorus organic builders useful herein include the various alkali metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates and polyhydroxy sulfonates. Examples of polyacetate and polycarboxylate builders are the sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylene diamine tetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, and citric acid.

Polymeric polycarboxylate builders are set forth in U.S. Patent 3,308,067, Diehl, issued March 7, 1967, the disclosure of which is incorporated herein by reference. Such materials include the water-soluble salts of homo- and copolymers of aliphatic carboxylic acids such as maleic acid, itaconic acid, mesaconic acid, fumaric acid, aconitic acid, citraconic acid and methylenemalononic acid. Some of these materials are useful as the water-soluble anionic polymer as hereinafter described, but only if in intimate admixture with the non-soap anionic surfactant.

Other suitable polycarboxylates for use herein are the polyacetal carboxylates described in U.S. Patent 4,144,226, issued March 13, 1979 to Crutchfield et al, and U.S. Patent 4,246,495, issued March 27, 1979 to Crutchfield et al, both of which are incorporated herein by reference. These polyacetal carboxylates can be prepared by bringing together under polymerization conditions an ester of glyoxylic acid and a polymerization initiator. The resulting polyacetal carboxylate ester is then attached to chemically stable end groups to stabilize the polyacetal carboxylate against rapid depolymerization in alkaline solution, converted to the corresponding salt, and added to a detergent composition. Particularly preferred polycarboxylate builders are the ether carboxylate builder

compositions comprising a combination of tartrate monosuccinate and tartrate disuccinate described in U.S. Patent 4,663,071, Bush et al., issued May 5, 1987, the disclosure of which is incorporated herein by reference.

Water-soluble silicate solids represented by the formula  $\text{SiO}_2 \cdot \text{M}_2\text{O}$ , M being an alkali metal, and having a  $\text{SiO}_2:\text{M}_2\text{O}$  weight ratio of from about 0.5 to about 4.0, are useful salts in the detergent granules of the invention at levels of from about 2% to about 15% on an anhydrous weight basis, preferably from about 3% to about 8%. Anhydrous or hydrated particulate silicate can be utilized, as well.

The starting or entering detergent components in the present process can also include any number of additional ingredients. These include other detergency builders, bleaches, bleach activators, suds boosters or suds suppressors, anti-tarnish and anticorrosion agents, soil suspending agents, soil release agents, germicides, pH adjusting agents, non-builder alkalinity sources, chelating agents, smectite clays, enzymes, enzyme-stabilizing agents and perfumes. See U.S. Patent 3,936,537, issued February 3, 1976 to Baskerville, Jr. et al., incorporated herein by reference.

Bleaching agents and activators are described in U.S. Patent 4,412,934, Chung et al., issued November 1, 1983, and in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, both of which are incorporated herein by reference. Chelating agents are also described in U.S. Patent 4,663,071, Bush et al., from Column 17, line 54 through Column 18, line 68, incorporated herein by reference. Suds modifiers are also optional ingredients and are described in U.S. Patents 3,933,672, issued January 20, 1976 to Bartoletta et al., and 4,136,045, issued January 23, 1979 to Gault et al., both incorporated herein by reference.

Suitable smectite clays for use herein are described in U.S. Patent 4,762,645, Tucker et al., issued August 9, 1988, Column 6, line 3 through Column 7, line 24, incorporated herein by reference. Suitable additional detergency builders for use herein are enumerated in the Baskerville patent, Column 13, line 54 through Column 16, line 16, and in U.S. Patent 4,663,071, Bush et al, issued May 5, 1987, both incorporated herein by reference.

In order to make the present invention more readily understood, reference is made to the following examples, which are intended to be illustrative only and not intended to be limiting in scope.

#### EXAMPLE I

This Example illustrates the process of the invention which produces free flowing, high density detergent agglomerates. A batch version of the present process is described hereinafter. Initially, a surfactant paste, sodium salt of a copolymer of maleic and acrylic acid (10% by weight, hereinafter referred to as "copolymer"), anhydrous material (magnesium sulfate), and an aqueous solution containing 32% by weight of the sodium salt of ethylene diamine-N, N-disuccinic acid (hereinafter referred to as "chelant") are added to the lab-scale planetary mixer. The surfactant paste comprises an aqueous paste composition comprising 78% by weight of  $\text{C}_{12-15}$  alkyl sulfate

and C<sub>13-15</sub> alkyl ethoxy sulfate in a ratio of 80:20, and 20% water. 200 grams of a powdered builder mixture (hereinafter referenced as the "builder") comprising zeolite A and sodium carbonate in a weight ratio of 1:1 (90% by weight) is added into a lab-scale high shear mixer (Braun™). Thereafter, the surfactant paste (at 50°C) is continuously fed into the high shear mixer/densifier at a rate of 500 g/min until agglomerates are produced. The resulting detergent agglomerates have a density in a range from about 700 to 750 g/l and a mean particle size between about 400 to about 600 microns.

Compositions A, B, C, D, E and F are made according to the process described above and represent the composition of the starting ingredients prior to agglomeration in the high shear mixer, the relative proportions of which are presented in Table I:

TABLE I

% Weight

	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>
Surfactant Paste	71	68	64	95	90	85
Copolymer	17	16	15	-	-	-
Chelant	7	6	6	-	-	-
Anhydrous(MgSO <sub>4</sub> )	<u>5</u>	<u>10</u>	<u>15</u>	<u>5</u>	<u>10</u>	<u>15</u>
	100	100	100	100	100	100

Subsequent to agglomeration in the high shear mixer, final detergent agglomerates for each of compositions A-F are produced. The amount of surfactant ("activity") in the resulting detergent agglomerate compositions A-F for residence times in the mixer of 1 minute and 5 minutes is presented in Table II.

TABLE II

Surfactant Level (% weight)

Residence Time	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>
1 minute	35%	39%	42%	41%	43%	44%
5 minutes	37%	41%	44%	43%	45%	46%

As can be seen from Table II, an increase in residence time in the planetary mixer has a tendency to increase the surfactant level in the final detergent agglomerates, a feature particularly useful in the production of low dosage detergents.

## EXAMPLE II

This Example provides a comparison with Example I and demonstrates the reduced surfactant levels in detergent agglomerates produced by a process outside the scope of the invention. The detergent agglomerates in this Example are made by a process which does not include the step of adding an anhydrous material. In composition G, only surfactant paste is fed (500 g/min at 50°C) into the high shear mixer which contains 200 grams of the builder mixture. In composition H, surfactant paste, copolymer and chelant are added to the high shear mixer as described in

Example I. The proportions of ingredients added to the high shear mixer for compositions G and H are presented in Table III:

TABLE III

% Weight

5

	<u>G</u>	<u>H</u>
Surfactant Paste	100	75
Copolymer	-	18
Chelant	<u>=</u>	<u>7</u>
	100	100
Surfactant level	40%	35%

Starting compositions G and H are agglomerated in the high shear mixer as described in Example I to a density of from 700 to 750g/l and a mean particle size between 400 and 600 microns. As presented in Table III, the resulting detergent agglomerates have surfactant levels of 40% and 35% for the compositions G and H, respectively. These levels are considered substantially lower than the surfactant levels achieved by the detergent agglomerates made in accordance with the invention in Example I. Accordingly, the inclusion of an anhydrous material just prior to agglomeration effectively increases the surfactant level in the resulting detergent agglomerates (Example I), while omission of the step of adding an anhydrous material as described in this Example does not yield the desired higher surfactant levels in the final detergent agglomerates.

Having thus described the invention in detail, it will be obvious to those skilled in the art that various changes may be made without departing from the scope of the invention and the invention is not to be considered limited to what is described in the specification.

## WHAT IS CLAIMED IS:

1. A process for preparing high density detergent agglomerates characterized by the steps of:
  - (a) charging a viscous surfactant paste into a mixer/densifier wherein said surfactant paste has a viscosity of from 5,000 cps to 100,000 cps and contains from 70% to 95%, by weight of said surfactant paste, of a deterative surfactant and the balance water;
  - (b) adding from 1% to 70% by weight of an anhydrous material selected from the group consisting of carbonates, sulfates, carbonate/sulfate complexes, tripolyphosphates, tetrasodium pyrophosphate, citrates, aluminosilicates, cellulose-based materials and organic synthetic polymeric absorbent gelling materials into said surfactant paste just prior to entrance into said mixer/densifier to absorb at least a minor amount of said water from said surfactant paste; and
  - (c) agglomerating said surfactant paste and said anhydrous material by treating said surfactant paste and said anhydrous material initially in a high speed mixer/densifier and subsequently in a moderate speed mixer/densifier so as to form detergent agglomerates having a density of at least 650 g/l.
2. A process according to claim 1 further characterized by the step of drying said detergent agglomerates.
3. A process according to claims 1-2 wherein said surfactant paste comprises a surfactant selected from the group consisting of anionics, cationics, nonionics and mixtures thereof, and water.
4. A process according to claims 1-3 further characterized by the step of adding an additional binder to said mixer/densifier during said agglomerating step.
5. A process according to claims 1-4 wherein said additional binder is selected from the group consisting of water, anionic surfactants, nonionic surfactants, polyethylene glycol, polyacrylates, citric acid and mixtures thereof.
6. A process according to claims 1-5 wherein said agglomerates have a surfactant level of from 25% to 55% by weight.
7. A process according to claims 1-6 wherein said anhydrous material is selected from the group consisting of carbonates, sulfates, carbonate/sulfate complexes, and mixtures thereof.
8. A process according to claims 1-7 wherein said surfactant paste has a viscosity of from 7,500 cps to 75,000 cps.

-15-

9. A process according to claims 1-8 wherein said agglomerates have a mean particle size of from 400 microns to 600 microns.

10. A process according to claims 1-9 wherein said anhydrous material is selected from group characterized by organic synthetic polymeric absorbent gelling materials, cellulose-based materials and combinations thereof.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 94/08957A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C11D17/06 C11D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 508 543 (PROCTER & GAMBLE) 14 October 1992 see column 4, line 37 - column 5, line 13 see column 6, line 42 - line 52 see column 8, line 13 - column 11, line 33 see column 15, line 45 - column 18, line 22; claim 1; examples 1-3 ---	1-5,7,8
X	EP,A,0 510 746 (PROCTER & GAMBLE) 28 October 1992 see page 8, line 46 - page 10, line 11; claims 1,4-6; examples 1-3 ---	1-5,7,8
X	EP,A,0 349 200 (PROCTER & GAMBLE) 3 January 1990 see page 7, line 12 - line 43; claims 1,2,6; example 1 --- -/--	1-5,7,8

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

\*&amp;\* document member of the same patent family

Date of the actual completion of the international search

16 December 1994

Date of mailing of the international search report

28.12.94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Van Bellingen, I

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 94/08957

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 349 201 (PROCTER & GAMBLE) 3 January 1990 see page 6, line 40 - page 8, line 11; claims 1,4 -----	1-5,7,8

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US 94/08957

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0508543	14-10-92	AU-A- 1870092	17-11-92
		CA-A- 2108166	13-10-92
		CN-A- 1066881	09-12-92
		JP-T- 6506719	28-07-94
		NO-A- 933641	13-12-93
		WO-A- 9218602	29-10-92
EP-A-0510746	28-10-92	AU-A- 1878592	17-11-92
		CA-A- 2108167	13-10-92
		CN-A- 1067674	06-01-93
		JP-T- 6506720	28-07-94
		NO-A- 933642	13-12-93
		WO-A- 9218603	29-10-92
EP-A-0349200	03-01-90	US-A- 4925585	15-05-90
		US-A- 5080848	14-01-92
		AU-B- 624155	04-06-92
		AU-A- 3713589	04-01-90
		CA-A- 1325944	11-01-94
		CN-B- 1024357	27-04-94
		EP-A- 0349201	03-01-90
		JP-A- 2086700	27-03-90
		JP-A- 4081500	16-03-92
		CN-B- 1024356	27-04-94
EP-A-0349201	03-01-90	US-A- 4925585	15-05-90
		AU-B- 624155	04-06-92
		AU-A- 3713589	04-01-90
		CA-A- 1325944	11-01-94
		CN-B- 1024357	27-04-94
		EP-A- 0349200	03-01-90
		JP-A- 2086700	27-03-90
		JP-A- 4081500	16-03-92